

REMARKS

Claims 43-64 and 66-75 are currently pending in the present application. Claims 55-58, 61-64, and 66-75 are withdrawn due to restriction requirement. Claim 65 is canceled herein without admission or prejudice. Claims 43, and 66-69 are currently amended herein for clarification. Support for the amendment to claim 43 is provided in the application, for example, in canceled claim 65. With the amendment, it is believed that independent claim 43 remains generic for all species. It is believed that no new matter has been entered.

Claims 43-54, 59 and 60 were rejected under 35 U.S.C. 103(a) as being unpatentable over Kuylenstierna et al ("Tuneable Electromagnetic Bandgap Structures Based on $\text{Ba}_{0.25}\text{Sr}_{0.75}\text{TiO}_3$ Parallel-Plate Varactors on Silicon Coplanar Waveguides") in view of Satoh et al (US 5,576,564). Claims 43-48, 52-54, 59, and 60 were rejected under 35 U.S.C. 103(a) as being unpatentable over Satoh in view of Mueller et al (US 6,097,263). These rejections are respectfully traversed.

None of the references (Kuylenstierna, Mueller, or Satoh) teach or suggest a varactor comprising, *inter alia*, a top metal electrode, wherein said top metal electrode comprises at least two ground conductors and a central signal strip. Such a feature is neither disclosed nor suggested by the cited references, and thus should overcome the stated rejection.

In addition to these deficiencies, the combination of Satoh and Mueller also fails to teach or suggest, *inter alia*, a tunable ferroelectric thin-film dielectric layer having a dielectric constant of greater or equal to about 200 at zero bias, and an optimized dielectric constant of 1200. The material used by Satoh et al is $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ which is a ferroelectric with a hysteresis loop describing the ferroelectric behavior of the material (figure 6, Satoh et al.). Typically, the ferroelectric materials with a hysteresis behavior exhibit dispersive dielectric properties (dielectric properties vary as a function of frequency). Macedo¹ et al published a paper showing the dielectric properties of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ material as a function of frequency. As stated in Macedo,

The data revealed a remarkable dielectric relaxation at ~ 500 kHz independently of the power level condition. It is also verified in figure 4(a) that the relaxation strength ($\Delta\epsilon'$) is higher for higher laser powers and ϵ''

¹ Macedo et al., "Dielectric and Ferroelectric Properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics produced by a laser sintering method," J. of Physics: Condensed Matter, vol. 16, pp. 2811-28, 2004.

always reaches **almost the same value** ($\epsilon' \approx 220$) after the relaxation process. At low frequencies ϵ'' (loss) increases considerably due to dc conductivity contribution. The fact that all dielectric relaxations occur at the same frequency allows us to suppose the existence of a unique mechanism responsible for the relaxations [25]. Although these dielectric measurements are not able to identify precisely the mechanism involved in this process, space charges, mainly oxygen vacancies, are possible candidates due to their relatively high mobility [26, 27].²

Consequently, because of the hysteresis loop, there is no teaching or suggestion that the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ material could achieve a dielectric constant of greater or equal to about 200 at zero bias, and an optimized dielectric constant of 1200. In fact, when viewing the teachings of the Macedo, specifically, the hysteresis loop and relaxation permittivity of 220 for $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, Macedo teaches away from a finding that a dielectric constant of greater or equal to about 200 at zero bias, and an optimized dielectric constant of 1200 is inherently achievable. "To establish inherency, the extrinsic evidence 'must make clear that the missing descriptive matter is **necessarily present** in the thing described in the reference" *In re Robertson*, 169 F.3d 743, 745, 49 USPQ2d 1949, 1950-51 (Fed. Cir. 1999). As there is no teaching that these claimed dielectric constant values are necessarily present, Satoh fails to teach or suggest, *inter alia*, a tunable ferroelectric thin-film dielectric layer with a dielectric constant of greater or equal to about 200 at zero bias, and an optimized dielectric constant of 1200 as recited in claim 43. Mueller, which fails to disclose varactor shunt switches, fails to cure the above noted deficiencies of Satoh.

As a result, the rejections are believed to be traversed and reconsideration is respectfully requested.

Conclusion

Applicants respectfully submit that, the currently pending claims represent allowable subject matter. Applicants respectfully request rejoinder of all non-elected claims upon the allowance of elected claims. The Examiner is encouraged to contact the undersigned to resolve

² *Id.* at figure 4, pp. 2816, emphasis provided.

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efficiently any formal matters or to discuss any aspects of the application or of this response.
Otherwise, early notification of allowable subject matter is respectfully solicited.

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Dielectric and ferroelectric properties of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics produced by a laser sintering method

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Abstract

This work reports the synthesis and electrical characterization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics produced successfully by a new method based on a CO_2 laser sintering process. The structural and microstructural characterizations revealed that this method is able to produce sintered samples with high quality, free from secondary phases and with density as high as 98% of the theoretical one. Additionally, ferroelectric and dielectric investigations also revealed excellent values for the polarization and dielectric constant, respectively, thus showing the viability of the proposed method.

1. Introduction

Over the last few decades ferroelectric materials have been intensively investigated due to their remarkable physical properties of practical interest. For instance, ferroelectric thin films as well as bulk ceramics have had a strong impact in a large number of technological applications such as in ferroelectric memories [1] and piezoelectric devices [2].

Bismuth titanate ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) is a ferroelectric material with layered structure belonging to the Aurivillius family [3], which has undoubtedly emerged as a high quality material due to its excellent electrical and electromechanical properties. Indeed, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ has a strong potential for being employed in many electronic devices because of its relatively high Curie temperature (T_c), high dielectric breakdown strength, low dielectric loss and high anisotropy. The polarization axis forms an angle of $\sim 4.5^\circ$ with the crystallographic plane **ab** [4], so the higher component of the spontaneous polarization is parallel to the bismuth layers [5]. However, in order to optimize the physical properties of ferroelectric ceramics, it is a fundamental requirement to control the synthesis and sintering parameters that affect

their microstructure. Indeed, it is well known that microstructure plays an important role in understanding and improving the electrical properties of ferroelectric materials for several practical purposes. The purity of precursor powders, size of grains and morphology, pressing of the compacts and the thermal cycle adopted for sintering are some of the parameters involved in the quality of the final product. In this context, many preparation processes have been developed to optimize the microstructure and to produce ceramics with high density and free from secondary phases [6].

In the last few years, laser technology has been employed in an increasing variety of processes. For instance, laser heating can be controlled for use in cutting, soldering, ablation and coating [7, 8]. Moreover, the use of lasers as heating sources for calcination and melting of materials [9] as well as for growth of crystalline fibres [10] has remarkably presented a reduced risk of contamination, since the procedures are performed quickly and avoid contact of the material with crucibles and furnaces. The potential use of lasers for deposition, sintering and texturing of thin films [11, 12] and for crystallization of glasses [13] has also been widely investigated. As regards laser sintering, this technique has been largely employed in so-called selective laser sintering, in which only some parts of the compact are heated and sintered [14]. However, the process of sintering of an entire bulk ceramic has received less attention up to now, mainly because the first tests registered the existence of microstructural damage in the sintered bodies [15]. Nevertheless, it has been shown in our previous work that the damage can be controlled successfully through a suitable sintering procedure [16]. Our results revealed that laser sintering yields excellent pore shrinkage and highly dense compacts.

The objective of this work is to report the production and the electrical characterization of bismuth titanate ceramics sintered through the CO₂ laser sintering process. The influence of this new sintering process on the microstructure as well as on the ferroelectric and dielectric properties is discussed.

2. Experimental details

Solid-state reaction was employed to synthesize single-phase Bi₄Ti₃O₁₂ ceramics (BIT). The precursor powders Bi₂O₃ and TiO₂ (Alfa Aesar, 4N), employed in the stoichiometric proportions, were ball-milled for 3 h, calcined at 800 °C for 3 h, milled again for 108 h and calcined at 800 °C for 10 h more. After the last calcination the powder was milled again for 24 h more to prevent some undesirable grain growth processes that can start during the calcination step. The as-dried material was then mixed with a binder solution of polyvinyl alcohol with the concentration of 0.1 g ml⁻¹ and formed via uniaxial pressing under 25 MPa into the form of discs with 6 mm diameter and 1 mm thickness.

The laser sintering process employed a continuous CO₂ laser (Synrad 57-1) as the main heat source. The laser beam had a diameter of 4.0 ± 0.5 mm, which was maintained fixed on the centre of the sample throughout the sintering process. Before the irradiation, the pellets were heated up to 350 °C at a heating rate of about 50 °C min⁻¹ and kept at this temperature during the laser sintering. After this pre-heating, the power was raised at a linear rate of 2.7 W min⁻¹, up to 5 W, maintained at this level for 5 min and then raised again at the same rate up to a maximum value that we have called P_{max} . After irradiating the first face, the entire process was repeated on the other side. P_{max} values between 10 and 30 W were tested. It must be emphasized that the average time of the laser sintering process employed in this work is around 20 min, which is almost ten times shorter than the conventional sintering.

Structural and phase characterizations of the calcined powder were done by means of x-ray diffraction (XRD) in a Rigaku Rotaflex RU-200B, using K α radiation from Cu. The measurements were performed from 10° to 80° in steps of 0.02° and acquisition times of 3 s. The patterns were analysed by the software Fullprof [17]. The XRD of the laser sintered

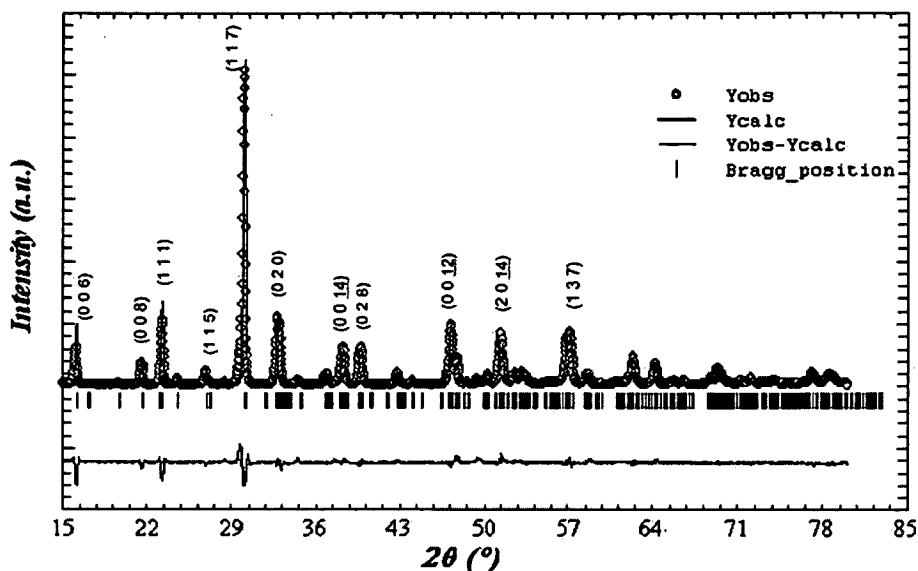


Figure 1. Plot output from the Rietveld refinement of the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ calcined powder. The dots represent the XRD data and the solid curve represents the calculated pattern. The difference plot is shown at the bottom of the graph. Some crystalline planes are indexed.

samples was measured in continuous scanning mode from 5° to 80° and at a scanning rate of 2° min^{-1} . A Zeiss DSM960 scanning electron microscope (SEM) was used to analyse the microstructure of the sintered materials. The bulk density of the ceramics was determined by using ASTM procedure C373, which is based on Archimedes' principle. Firstly, the dry mass was measured and then the samples were kept for 2 h in distilled water at 100°C , so the open pores were saturated with water. After that, the net saturated suspended weight, corresponding to the volume of fluid displaced, was determined. The density was determined as the ratio between the dry mass and the volume of fluid displaced, and the relative density was the ratio between the measured and theoretical density.

For the ferroelectric characterization, BIT ceramics in the disc shape were polished to a thickness of 0.5 mm with silicon carbide and alumina powder, cleaned in an ultrasonic bath in isopropilic alcohol and thermally treated at 700°C to release stresses introduced during the polishing. After that, the parallel faces were painted with Ag paste and treated at 300°C for 30 min. Ferroelectric hysteresis measurements were made at room temperature employing a system based on a Sawyer–Tower circuit [18] applying a triangular electric field of amplitude of 75 kV cm^{-1} at 10 Hz. This low frequency value was adopted in order to avoid the heating of the sample, which can change the ferroelectric response [19]. For dielectric measurements, the parallel faces of the ceramic discs, polished as described above, were painted with Pt paste and fired at 700°C for 30 min. The measurements were performed isothermally, in the frequency range from 5 Hz to 13 MHz, with an applied potential of 500 mV, using a Solartron 1260 Impedance Analyzer.

3. Results and discussions

The x-ray diffraction patterns of the calcined powder presented a single-crystalline phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, as one can see in figure 1. The Rietveld refinement of the pattern confirmed an

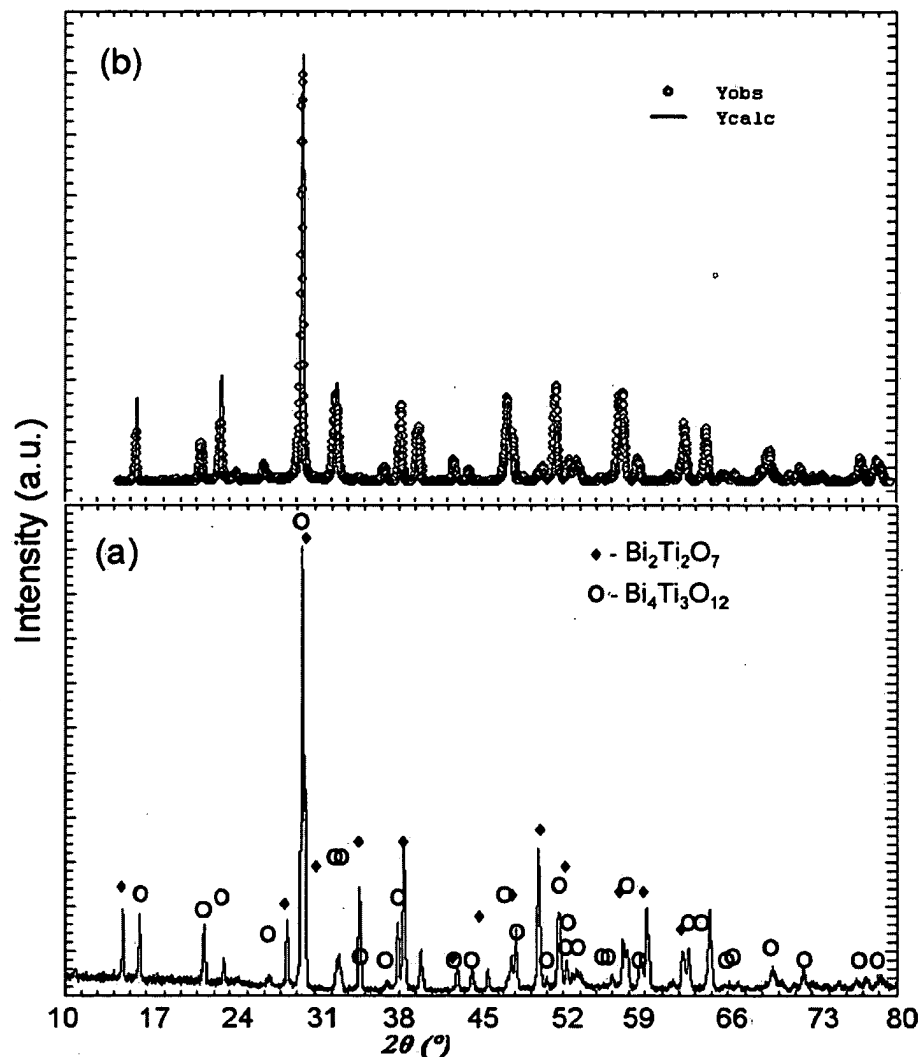


Figure 2. (a) XRD patterns of the laser sintered BIT ceramics indexed using the JCPDS-ICDD files; (b) the refined pattern of the laser sintered ceramic after thermal treatment at 700 °C and slow cooling down to RT.

orthorhombic structure and spatial group $B2cb$ at room temperature, as previously reported in [20] and [21]. The fitting employed a pseudo-Voigt function and the calculated cell parameters were $a = 5.4486 \text{ \AA}$, $b = 5.4085 \text{ \AA}$ and $c = 32.8386 \text{ \AA}$, with pattern deviation $R_p = 5$. These parameters are in good agreement with the values determined by Hervoches *et al* [21].

Figure 2(a) presents the XRD pattern of the laser sintered ceramics, which indicated a considerable portion of the phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ coexisting with the major phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. It has been reported that $\text{Bi}_2\text{Ti}_2\text{O}_7$ is an intermediate and unstable phase that occurs in the formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [22, 23]. In our samples, this phase was probably frozen during the fast cooling

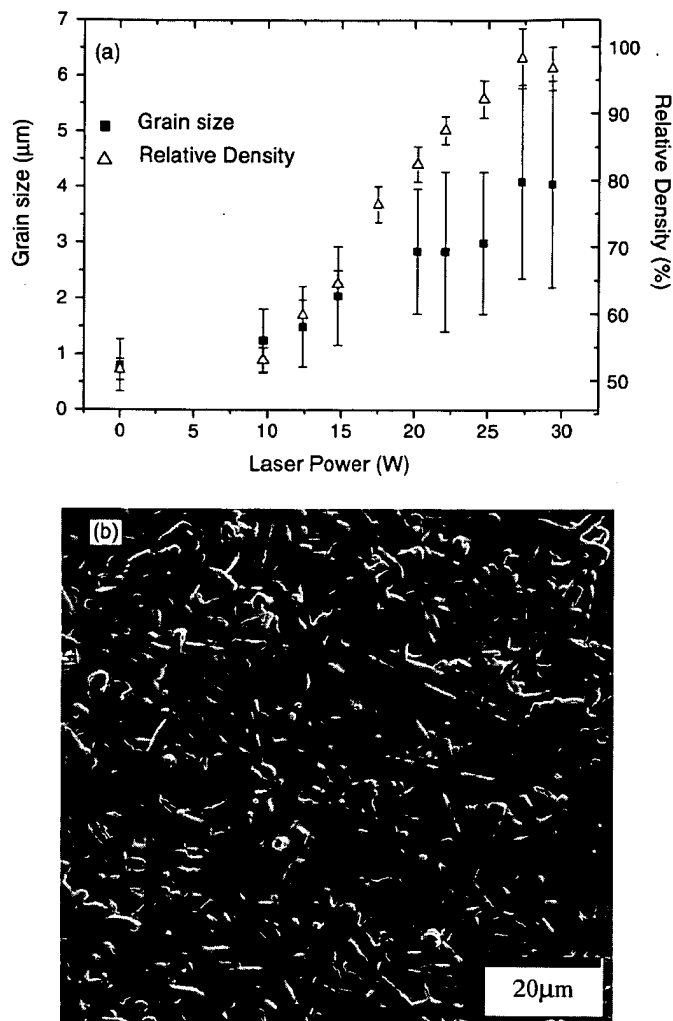


Figure 3. (a) The grain size and relative density of BIT ceramics sintered under various power values; (b) an SEM photograph showing the microstructure of a BIT ceramic sintered at 30 W for 5 min.

step of the laser sintering process. However, according to [24] the phase diagram of the $\text{Bi}_2\text{O}_3\text{--TiO}_2$ system the phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ can be converted into $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ at 700 °C. Indeed, the results revealed clearly that this conversion occurred in the samples annealed at 700 °C and slowly cooled down to room temperature (see figure 2(b)). Therefore, since all samples were heated up to 700 °C after the polishing, the phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ was eliminated and the measured ceramics presented only the phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The XRD pattern of the annealed ceramic was fitted to a pseudo-Voigt function (figure 2(b)), with the same cell parameters as determined for the conventional ceramic, and $R_p = 11$.

Figure 3(a) shows the relative density and the grain size dependence on the laser power intensity for the BIT ceramics. It was found that the density increased considerably when

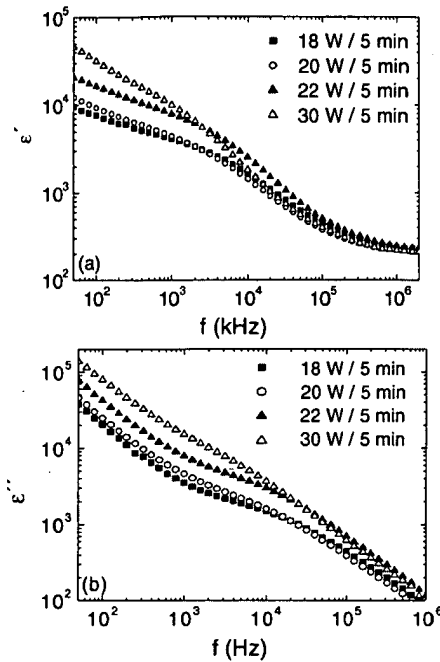


Figure 4. (a) Real (ϵ') and imaginary (ϵ'') components of the relative dielectric permittivity of BIT ceramics sintered under laser powers varying from 18 to 30 W, measured at 350 °C in the frequency interval from 100 Hz to 1 MHz.

power levels from 10 to 27 W were employed. For higher power values, the density of the sintered ceramics tends to level out at around 98% of the theoretical density. In accordance with the densification behaviour, it is also observed that the average grain size growth follows the same tendency as the density, stabilizing between 3 and 4 μm . Figure 3(b) presents a SEM image of the BIT ceramic sintered at 30 W.

Figures 4(a) and (b) show the frequency dependence of the real (ϵ') and imaginary (ϵ'') components of the relative dielectric permittivity for the BIT ceramics sintered under various power intensity conditions. These dielectric measurements were performed isothermally at 350 °C. The data revealed a remarkable dielectric relaxation at ~ 500 kHz independently of the power level condition. It is also verified in figure 4(a) that the relaxation strength ($\Delta\epsilon'$) is higher for higher laser powers and ϵ' always reaches almost the same value ($\epsilon' \approx 220$) after the relaxation process. At low frequencies ϵ'' (loss) increases considerably due to dc conductivity contribution. The fact that all dielectric relaxations occur at the same frequency allows us to suppose the existence of a unique mechanism responsible for the relaxations [25]. Although these dielectric measurements are not able to identify precisely the mechanism involved in this process, space charges, mainly oxygen vacancies, are possible candidates due to their relatively high mobility [26, 27].

Figure 5 shows the ferroelectric hysteresis loop measurements of the samples sintered under laser power intensity higher than 18 W. The data revealed that the remanent polarization (P_r) was significantly increased with increase of the laser power, reaching $P_r = 6.5 \mu\text{C cm}^{-2}$, while the coercive field stabilized at around 23.5 kV cm^{-1} just after 20 W. The highest

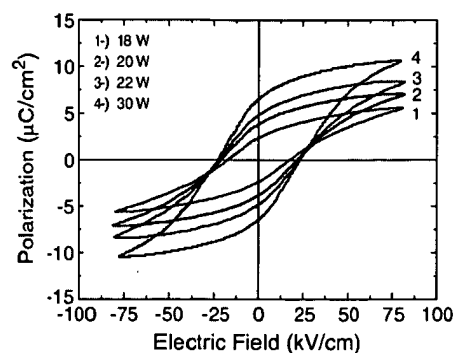


Figure 5. Ferroelectric hysteresis loops of BIT ceramics sintered under laser power varying from 18 to 30 W, measured at room temperature and at 10 Hz.

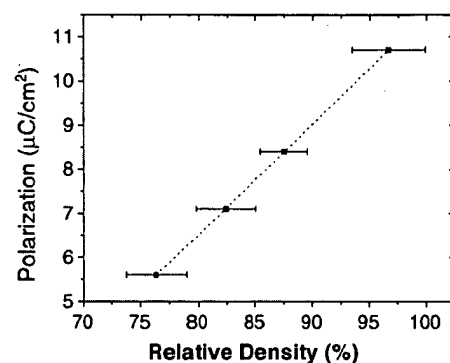


Figure 6. Polarization values as a function of the density of laser sintered BIT ceramics.

value found for P_r is higher than others commonly obtained for BIT ceramics produced by conventional sintering [28–30]. In accordance with the data in figure 6, it was verified that the increase in the polarization values was directly related to the enhancement in the density and pore shrinkage of ceramics sintered at higher power levels. The lower polarization values found for the less densified ceramics can be explained as due to the presence of a higher amount of space charges such as oxygen vacancies [31], which form depolarizing fields that decrease the polarization values [32, 33]. Although in some cases the polarization is also grain size dependent [34], it is believed that the grain size changes verified in figure 3(a) are not high enough to induce significant changes in the polarization. Much more variation in the average grain size is necessary to modify the domain configuration [35], thus changing the polarization values. Scanning electron microscopy analysis in figure 3(b) also revealed randomly oriented plate-like grains; thus the possible effect of texturization on the ferroelectric properties can be neglected.

4. Conclusions

In summary, this work reports the synthesis and the electrical characterization of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ceramics produced by the CO_2 laser sintering process. The results reveal that this new

method is able to produce highly dense and damage-free samples. The ferroelectric and dielectric characterizations showed that the samples reached high values for the polarization and dielectric constant, which demonstrated the viability of the proposed method. The electrical investigations suggest that higher space charge concentration occurs in samples sintered at lower laser power intensity.

Acknowledgments

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